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Molecular quadratic nonlinear optical properties of dipolar ruthenium(II) arsine complexes

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ABSTRACT

A series of complex salts in which *trans*-bis[1,2-phenylenebis(dimethylarsine)]chlororuthenium(II) electron donor groups are connected to pyridyl or pyridinium electron acceptors has been prepared. The chromophores in these compounds exhibit intense, visible metal-to-ligand charge-transfer (MLCT) absorptions and reversible Ru^{III/II} (and also in some cases ligand-based) redox processes. Stark (electroabsorption) spectroscopic studies have been used to determine dipole moment changes for the MLCT excitations. Static first hyperpolarizabilities β_0 have been calculated according to the two-state model, allowing the derivation of structure-activity correlations for the molecular quadratic nonlinear optical responses.

Keywords: Ruthenium complexes, pyridinium salts, Stark spectroscopy

1. INTRODUCTION

There is a strong likelihood that future optoelectronic and photonic data processing devices will be based on molecular materials which exhibit nonlinear optical (NLO) properties.¹⁻³ Recent fundamental research into such materials has increasingly included studies on organotransition metal complexes which can display very pronounced NLO effects, combined with various other potentially useful properties such as redox/magnetic behaviour.⁴⁻⁷ The derivation of detailed structure-activity correlations for first hyperpolarizabilities β , which govern molecular quadratic NLO effects, is the primary objective of most current work with such metal-based chromophores. Our contribution to this field has largely involved hyper-Rayleigh scattering (HRS)^{8,9} and Stark (electroabsorption)^{10,11} spectroscopic studies on a variety of Ru^{II} pyridyl ammine complexes containing pyridinium-substituted ligands.¹²⁻¹⁸ We have found that such dipolar chromophores can exhibit very large static first hyperpolarizabilities β_0 which are associated with intense, low energy metal-to-ligand charge-transfer (MLCT) transitions.¹²⁻¹⁸ The MLCT absorption and NLO properties of these complexes are highly tunable via judicious changes in ligand structure, in accordance with the widely used two-state model,^{19,20} and can also be readily and reversibly switched via the Ru^{III/II} redox couple.^{21,22}

Owing to continual difficulties with growing single crystals suitable for X-ray diffraction studies, we have obtained only very limited structural information on our Ru^{II} ammine complexes.^{12,14,15} Inspired by previous work with complexes of the chelating ligand 1,2-phenylenebis(dimethylarsine) (pdma),^{23,24} we have prepared a series of complexes featuring *trans*-{Ru^{II}Cl(pdma)₂}⁺ centres coordinated to our pyridinium ligands, with the original primary objective of gaining detailed crystallographic data. The syntheses, properties and crystal structures of some of these complexes have been previously described,²⁵ but without any accompanying NLO data. The reasons why no such data were originally obtained are: (i) MLCT absorption and electrochemical data clearly show that a *trans*-{Ru^{II}Cl(pdma)₂}⁺ centre is a considerably less effective electron-donor than an ammine-bearing unit such as {Ru^{II}(NH₃)₅}²⁺, implying that the β_0 values of the pdma complexes will be smaller than those of their ammine analogues; (ii) the MLCT bands of the pdma complexes lie very close to 532 nm, precluding the acquisition of meaningful HRS data with the standard 1064 nm Nd³⁺-YAG laser fundamental used to investigate the ammine complexes. However, since this previous study was reported,²⁵ we have carried out Stark spectroscopic measurements on our ammine complexes and found that this

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technique is a useful approach to deriving β_0 values for such MLCT-based chromophores.¹⁶⁻¹⁸ Although this Stark approach is indirect, the resonance effects which often limit the usefulness of direct HRS measurements are no longer a problem. Therefore, we have now synthesised several further novel dipolar Ru^{II} pdma complexes to expand the available series, and investigated the quadratic molecular NLO properties of these compounds by using Stark spectroscopy.

2. EXPERIMENTAL

2.1 General physical measurements

UV-visible spectra were obtained by using a Hewlett Packard 8452A diode array spectrophotometer, with acetonitrile as the solvent. Cyclic voltammetry was carried out with an EG&G PAR model 283 potentiostat/galvanostat. A single-compartment cell was used with a Ag-AgCl reference electrode, a Pt disc working electrode and a Pt wire auxiliary electrode. Acetonitrile was freshly distilled (from CaH₂) and NBu₄PF₆, twice recrystallized from ethanol and dried *in vacuo*, used as the supporting electrolyte. Solutions containing *ca.* 10⁻³ M analyte (0.1 M electrolyte) were deaerated by purging with N₂. All $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 200 mV s⁻¹.

2.2 Stark (electroabsorption) spectroscopy

The Stark apparatus, experimental methods and data analysis procedure were exactly as previously reported,^{16,26} with the only modification being that a xenon arc lamp was used as the light source in the place of a tungsten filament bulb. Butyronitrile was used as the glassing medium, for which the local field correction f_{int} is estimated as 1.33.^{16,26} The Stark spectrum for each compound was measured a minimum of three times using different field strengths, and the signal was always found to be quadratic in the applied field. Analysis of the Stark spectrum in terms of the Liptay treatment¹⁰ affords the dipole moment difference $\Delta\mu_{12}$, and the transition dipole moment μ_{12} can be determined from the oscillator strength f_{os} of the transition by

$$|\mu_{12}| = \left[f_{os} / (1.08 \times 10^{-5} E_{max}) \right]^{1/2} \quad (1)$$

where E_{max} is the energy of the MLCT maximum (in wavenumbers). If the first hyperpolarizability tensor β_0 has only nonzero elements along the MLCT direction, then this quantity is given by

$$\beta_0 = \frac{3\Delta\mu_{12}(\mu_{12})^2}{(E_{max})^2} \quad (2)$$

A relative error of $\pm 20\%$ is estimated for the β_0 values derived from the Stark data and using equation 2.

3. RESULTS AND DISCUSSION

3.1 Chromophore design and synthesis

We have prepared a series of dipolar complex salt chromophores having pyridyl or pyridinium electron acceptor groups linked to *trans*-bis[1,2-phenylenebis(dimethylarsine)]chlororuthenium(II) electron donors (Figure 1), with the primary intention of comparing the NLO and other molecular electronic properties of such compounds with those of complexes in which the same ligands are coordinated to Ru^{II} ammine centres. Complex salts **1-5** and **11-14** have been previously reported by ourselves,²³⁻²⁵ but **6-10** are new compounds.

Complex salt **6** was prepared via methylation of **4** with methyl iodide, whereas **7** was obtained directly by complexation of the pro-ligand salt [*N*-methyl-4-{*E,E*-4-(4-pyridyl)buta-1,3-dienyl}pyridinium] hexafluorophosphate¹⁷ with the sodium-azide treated complex precursor *trans*-[Ru^{II}Cl(pdma)₂(NO)]²⁺.²⁷ **8** was synthesized by reaction of the

corresponding *E,E,E*-1,6-bis(4-pyridyl)hexa-1,3,5-triene²⁸ complex with methyl iodide, and **9** was obtained from complexation of a *trans*-{Ru^{II}Cl(pdma)₂}²⁺ centre to bis(4-pyridyl)acetylene,²⁹ and then methylated to afford **10**. All compounds were characterized by using ¹H NMR spectroscopy and elemental analyses.

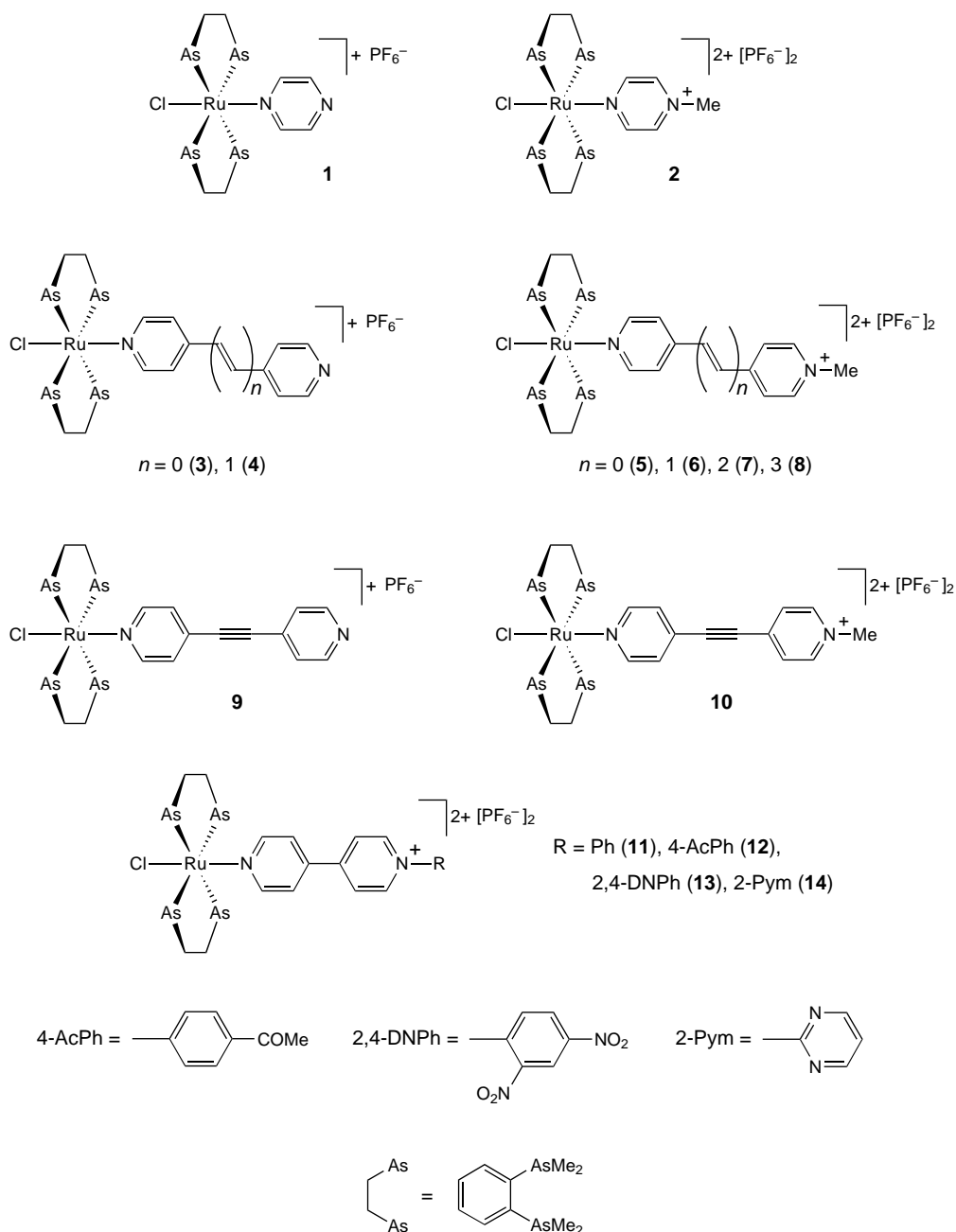


Figure 1. Chemical structures of the complex salts investigated.

3.2 Linear optical and electrochemical properties

The electronic absorption spectra of complex salts **1-14** all display intense, visible MLCT bands, and cyclic voltammetric studies reveal reversible or quasi-reversible Ru^{III/II} oxidation waves, together with pyridyl ligand first reduction processes which are reversible only for **2**, **4** and most of the 4,4'-bipyridinium-based species. Intense UV

absorptions due to intraligand $\pi \rightarrow \pi^*$ transitions are also observed. The MLCT absorption and electrochemical data for complex salts **1-14** are presented in Table 1.

Table 1. MLCT absorption and cyclic voltammetric data for complex salts **1-14**.^a

Salt	λ_{\max}^b [nm]	E_{\max}^b [eV]	ϵ^b [M ⁻¹ cm ⁻¹]	E [V vs. Ag-AgCl] (ΔE_p [mV]) ^c $E_{1/2}[\text{Ru}^{\text{III/II}}]$ $E_{1/2}[\text{L}^{+/0}]$ or E_{pc}^d
1 ^e	422	2.94	6100	1.22 (70) -1.48 ^d
2 ^e	558	2.22	12000	1.48 (75) -0.35 (65)
3 ^f	418	2.97	8400	1.10 (60) -1.49 ^d
4 ^f	434	2.86	14300	1.08 (60) -1.33 (60)
5 ^g	486	2.55	8300	1.14 (70) -0.74 (80)
6	492	2.52	13000	1.10 (95) -0.79 ^d
7	486	2.53	15700	1.09 (105) -0.80 ^d
8	472	2.58	15000	1.07 (110) -0.80 ^d
9	434	2.86	6000	1.12 (95) -1.10 ^d
10	488	2.54	11500	1.15 (105) -0.98 ^d
11 ^g	510	2.43	12500	1.15 (80) -0.58 (80)
12 ^g	520	2.38	10000	1.15 (85) -0.51 (90)
13 ^g	536	2.31	10400	1.16 (85) -0.38 ^d
14 ^g	544	2.28	10400	1.16 (80) -0.34 (90)

^a In acetonitrile solutions at 293 K. ^b Solutions *ca.* 10⁻⁵ M. ^c Solutions *ca.* 10⁻³ M in analyte and 0.1 M in NBu₄PF₆ at a platinum bead/disc working electrode with a scan rate of 200 mV s⁻¹. Ferrocene internal reference $E_{1/2} = 0.43$ V, $\Delta E_p = 60$ -110 mV. ^d For an irreversible reduction process. ^e Ref. 23. ^f Ref. 24. ^g Ref. 25.

As expected, methylation of the uncoordinated pyridyl nitrogen in **1**, **3**, **4** or **9** (to give **2**, **5**, **6** or **10**, respectively) leads to large red-shifts in the MLCT bands (Table 1). The electrochemical data reveal that these shifts arise primarily from stabilisation of the ligand-based LUMOs, but the Ru-based HOMO also shows some stabilisation, especially on moving from **1** to **2** in which the extent of electronic coupling between the pyridinium nitrogen and the Ru centre is expected to be the largest amongst the complexes studied.

Within the polyene series **5-8**, an initial red-shift of the MLCT band occurs on moving from $n = 0$ to 1, but the MLCT energy E_{\max} increases slightly as the chain is further extended up to three *E*-ethylene units (Table 1). This is highly unusual optical behaviour because the intramolecular charge-transfer (ICT) bands of donor-acceptor polyene chromophores almost always *red-shift* on chain elongation, irrespective of whether terminal metal centres are present.³⁰⁻³⁴ As far as we are aware, the only previous reports of donor-acceptor polyenes in which the ICT/MLCT bands blue-shift with increasing conjugation length involve compounds having tetrathiafulvalenyl (TTF) donor groups with various strong electron acceptors including 2,2-dicyanovinyl,³⁵ and also complexes related to **5-8**, but containing Ru^{II} ammine centres, recently studied in our laboratory.¹⁷

Within the 4,4'-bipyridinium-based series **5** and **11-14**, E_{\max} decreases steadily as the *N*-pyridinium substituent changes in the order R = Me > Ph > 4-AcPh > 2,4-DNPh > 2-Pym (Table 1). Similar behaviour has been observed in Ru^{II} ammine complexes of the same ligands,^{14,15} and this trend is attributable largely to a continual stabilisation of the ligand-based LUMO as the electron-withdrawing ability of R increases, as reflected in the ligand first reduction potentials (Table 1).

3.3 Stark spectroscopic studies and molecular quadratic NLO properties

We have carried out Stark spectroscopic studies with complex salts **1-8** and **10-14** in butyronitrile glasses at 77 K, and the results are presented in Table 2. Satisfactory data fits could only be obtained for the MLCT bands. As observed previously with Ru^{II} amines,^{16-18,26} the E_{\max} values generally decrease on moving from acetonitrile solution to butyronitrile glass (Tables 1 and 2), but an opposite effect is observed for **2**. Within the polyene series **5-8**, the $\Delta\mu_{12}$ values increase steadily with n , as is normal for donor-acceptor polyenes, whilst a large increase in μ_{12} is observed on

moving from $n = 1$ to 2 (Table 2). It is reasonable to assume that the lowest energy (*i.e.* MLCT) electronic absorption bands will dominate the NLO responses of the chromophores under study, so β_0 values have been derived from equation 2. The β_0 values for **5-8** appear to increase on moving from $n = 0$ to 3, but the large estimated relative error ($\pm 20\%$) on these numbers means that the values for the pairs **5/6** and **7/8** may not be significantly different.

As expected, increasing the electron acceptor strength by *N*-methylation of **1**, **3** and **4** leads to increases in β_0 , the effect being largest in the pyrazine complexes. Within the 4,4'-bipyridinium-based series **5** and **11-14**, β_0 increases steadily (Table 2), with a *ca.* 2-fold total enhancement on replacing a *N*-Me with a *N*-(2-Pym) substituent. As expected according to the two-state model, this trend parallels the red-shifting of the MLCT bands, and similar behaviour of β_0 has been observed in the related Ru^{II} ammine complexes of the same ligands.^{14,15}

Table 2. MLCT absorption and Stark spectroscopic data for complex salts **1-8** and **10-14**.^a

Salt	λ_{\max} [nm]	E_{\max} [eV]	μ_{12}^b [D]	$\Delta\mu_{12}^c$ [D]	β_0^d [10 ⁻³⁰ esu]
1	424	2.92	3.0	8.2	10
2	545	2.28	6.0	6.1	50
3	422	2.94	4.3	11.1 ^e	28
4	506	2.45	5.3	18.6	100
5	491	2.53	6.6	14.3	113
6	515	2.41	6.0	16.9	123
7	506	2.45	10.0	20.6	401
8	501	2.48	10.5	22.2	468
10	509	2.44	6.4	18.2	146
11	516	2.40	6.4	17.4	144
12	525	2.36	6.7	17.9	170
13	536	2.31	7.3	17.9	206
14	544	2.28	7.8	19.7	268

^a In butyronitrile glasses at 77 K. ^b Transition dipole moment derived from equation 1. ^c Dipole moment change calculated from $f_{\text{int}}\Delta\mu_{12}$ using $f_{\text{int}} = 1.33$. ^d Static first hyperpolarizability calculated from equation 2. ^e Inferior data fit.

3.4 Crystal structures

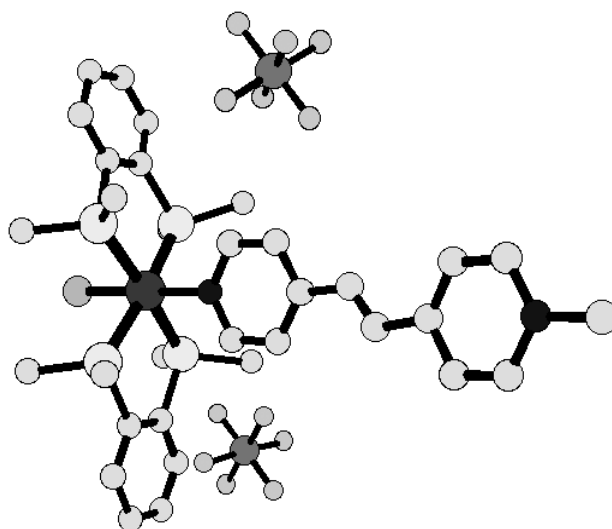


Figure 2. Representation of the molecular structure of the salt **6**, generated from X-ray crystallographic data.

Having investigated the molecular quadratic NLO properties of complex salts **1-8** and **10-14**, the next steps towards potentially useful materials are the preparation and study of crystalline samples in which bulk effects may be observed. We have previously determined single-crystal X-ray structures for a number of these complex salts, and found that the acetone solvate of **12** adopts the noncentrosymmetric orthorhombic space group $Pna2_1$.²⁵ We have also recently determined the structure of the new complex salt **6** (Figure 2), but this compound unfortunately crystallises centrosymmetrically in the monoclinic space group $P2_1/c$, precluding any bulk quadratic NLO effects.

3.5 Comparisons between ruthenium(II) arsine and ruthenium(II) ammine electron donor groups

Because the MLCT absorptions of $trans\text{-}\{\text{Ru}^{\text{II}}\text{Cl}(\text{pdma})_2\}^+$ complexes are found to high energy and have smaller molar extinction coefficients when compared with those of their Ru^{II} ammine analogues, we had previously assumed that such arsine complexes will have considerably smaller molecular quadratic NLO responses than the ammine species.²⁵ The new Stark spectroscopic data now available allow us to make direct quantitative comparisons to test this premise. Selected data for the two series of complex salts **5-8** and **11-13** and for their $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ analogues^{16,17} are presented in Table 3. Representative UV-visible absorption spectra of the $n = 2$ complex salt **7** and of its $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ analogue **7A** are shown in Figure 3.

Table 3. MLCT absorption and Stark spectroscopic data for salts **5-8**, **11-13** and their $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ analogues.^a

Salt ^b	λ_{max} [nm]	E_{max} [eV]	μ_{12} ^c [D]	$\Delta\mu_{12}$ ^d [D]	β_0 ^e [10 ⁻³⁰ esu]
5	491	2.53	6.6	14.3	113
5A ^f	645	1.92	5.2	13.8	120
6	515	2.41	6.0	16.9	123
6A ^f	681	1.82	5.5	16.2	175
7	506	2.45	10.0	20.6	401
7A ^g	675	1.84	7.9	22.4	482
8	501	2.48	10.5	22.2	468
8A ^g	669	1.85	7.2	27.1	475
11	516	2.40	6.4	17.4	144
11A ^f	696	1.78	5.7	15.3	186
12	525	2.36	6.7	17.9	170
12A ^f	718	1.73	5.8	17.0	229
13	536	2.31	7.3	17.9	206
13A ^f	731	1.70	5.8	16.3	225

^a In butyronitrile glasses at 77 K. ^b Analogous $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ complex salts denoted by **XA** (data for **14A** not available). ^c Transition dipole moment derived from equation 1. ^d Dipole moment change calculated from $f_{\text{int}}\Delta\mu_{12}$ using $f_{\text{int}} = 1.33$. ^e Static first hyperpolarizability calculated from equation 2. ^f Ref. 16. ^g Ref. 17.

In each case, the MLCT bands of the arsine complexes are blue-shifted by *ca.* 0.6 eV when compared with those of their pentaammine analogues at 77 K (Table 3). Previous comparative electrochemical studies have shown that this effect is largely attributable to a marked relative stabilisation of the Ru-based HOMOs in the arsine species.²⁵ Although the arsine complexes have *ca.* 40-50% lower molar extinction coefficients than their ammine counterparts at room temperature,²⁵ their μ_{12} values are actually higher in every case, since the band intensities increase substantially on freezing. The $\Delta\mu_{12}$ values do not show a consistent variation between the two types of complex chromophore, but are generally of similar magnitude (with the exception of those for **8** and **8A**). The values of β_0 , derived from equation 2, are slightly larger in each case for the ammine complex; although the actual differences are within the experimental error, the presence of a consistent trend is reasonably convincing evidence that the chromophores with $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ electron donors have the larger NLO responses, albeit only marginally so.

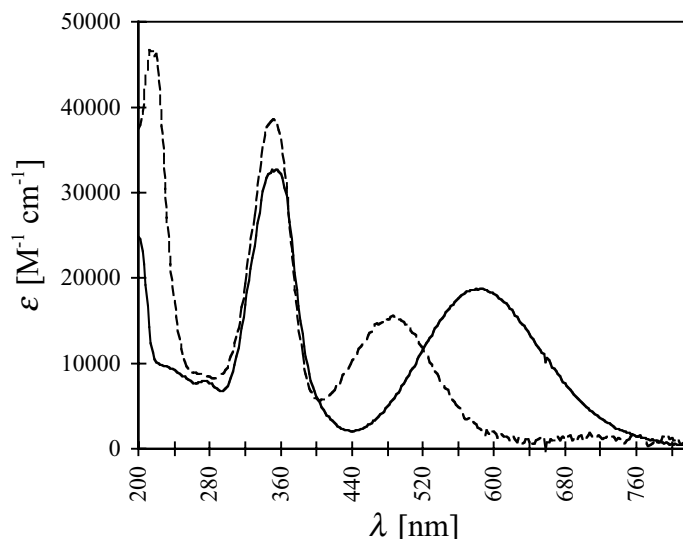


Figure 3. UV-visible absorption spectra of the salts **7** (dashed line) and **7A** (full line) at 293 K in acetonitrile.

4. CONCLUSIONS

MLCT absorption and electrochemical data clearly show that a $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ or related centre is more electron-rich than a $\text{trans-}\{\text{Ru}^{\text{II}}\text{Cl}(\text{pdma})_2\}^+$ unit. However, despite initial assumptions, analyses of Stark spectroscopic data according to the two-state model indicate that the β_0 responses of the arsine complexes are only a little smaller than those of their $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ analogues. Large molecular quadratic NLO responses have hence been maintained, with considerable gains in visible transparency, thermal stability and also crystallising ability. The unusual linear optical behaviour previously observed with pyridyl polyene complexes of Ru^{II} ammine centres is also found with the analogous arsine species, but clear evidence for a corresponding decrease in β_0 on chain extension is not observed.

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